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EP 0 339 909 A2 (54) Anti-fogging resin film-forming composition.

(57) An anti-fogging resin film-forming composition, comprising a block or graft copolymer and a surfactant, each of which block and graft copolymers consists of a hydrophilic polymer segment and a hydrophobic polymer segment having specifically limited monomer compositions, is disclosed. A coating film formed on a matrix surface from the composition has a durable excellent anti-fogging property and having high adhesion to the matrix surface and high strength.

ANTI-FOGGING RESIN FILM-FORMING COMPOSITION

This invention relates to an anti-fogging resin film-forming composition having a high strength in the resulting coating film and capable of protecting the surface of various materials and giving a permanent anti-fogging property to the polymer material surface.

Various plastic materials, glasses, transparent ceramics and mirror materials are widely used in various use fields, such as helmet shield, disaster-preventing mask, swimming goggles, mirror surface, lens of spectacles, film for agricultural house, packaging film for foods, window-glass of house, and the like, due to their excellent transparency and mirroring property. However, one of the serious drawbacks of these various materials is that, when they are used in a place kept to a high temperature and a high humidity or in a room kept to a temperature higher than that of the outdoor air, steam is condensed on the surface of these materials in the form of a fine waterdrop, and hence the surface of these materials is fogged.

In order to solve these drawbacks, various methods have been proposed. One of the methods is method (1), wherein a so-called composite film consisting of a polyester film and an anti-fogging film formed thereon or an acetyl cellulose film or the like, whose surface has previously been saponified, is stuck, for example, to a window glass of the building and house, and to a mirror in the bathroom and in the lavatory (Japanese Patent Application Publication No. 60-44,147, No. 60-44,148 and No. 60-44,149, and Japanese Patent Laid-open Specification No. 62-54,733). Further, as other methods, methods wherein a film having an anti-fogging property is formed on the surface of a transparent material. These methods are, for example, method (2), wherein a film consisting mainly of a hydrophilic polymer, such as a polymer of 2-hydroxyethyl methacrylate or polyvinyl alcohol, is formed on the surface of a transparent material (Japanese Patent Laid-open Specification No. 59-217,783 and No. 60-223,885); a method (3), wherein a film is formed on the surface of a transparent material by using a random copolymer consisting predominantly a hydrophilic polymer segment and containing a small amount of a hydrophobic polymer segments or a combination of the hydrophilic polymer and a surfactant in order to maintain the film strength against water (Japanese Patent Application Publication No. 52-47,754); a method (4), wherein a film of a mixture consisting of a hydrophilic and hydrophobic random copolymer and a surfactant is formed on a transparent material surface (Japanese Patent Laid-open Specification No. 56-62,856 and No. 57-98,518), and the like. Further, as a concrete embodiment, there is known a method, wherein an anti-fogging coating composition is coated on the surface of a polyester film, and then the anti-fogging coating composition is cured for a short time of about 10-180 seconds. As the treating condition in this case, there are known a method (5), wherein a mixture of a coating composition, which consists mainly of a hydrophilic polymer, such as a polymer of 2-hydroxyethyl methacrylate or polyvinyl alcohol, and an ion-hardenable crosslinking agent and occasionally a surfactant, is coated on a polyester film, and the coated polyester film is heat treated to form an anti-fogging coating film on the polyester film (Japanese Patent Laid-open Specification No. 59-15,473), and a method (b), wherein a coating composition consisting mainly of a free-radical reaction-inducing polyfunctional oligomer having polyethylene oxide chains in its molecule or 2-hydroxyethyl methacrylate and containing occasionally a surfactant is coated on a polyester film, and the coated polyester film is irradiated with a radiation or an ultraviolet ray to form an anti-fogging coating film on the polyester film (Japanese Patent Laid-open Specification No. 60-156,731).

However, the above described conventional methods have the following drawbacks. In the conventional method (1), the resulting hydrophilic cellulose film is poor in water resistance, heat resistance and brittle resistance, and wrinkles and bubbles are apt to be formed in the interface between the laminated cellulose film and polyester film, and hence the laminate can not be practically used. The conventional method (2) can form a somewhat satisfactory anti-fogging coating film, but the coating film is apt to be cracked and is poor in the strength, and moreover is poor in the adhesion to the surface of a matrix to be coated and is easily peeled off from the matrix. In the conventional method (3), although the coating film has satisfactorily improved strength and adhesion, the coating film is poor in the anti-fogging property, the improvement of which property is an important object of the present invention. In the conventional method (4), although the coating film has initially a high anti-fogging property, but the anti-fogging property decreases with the lapse of time, and moreover the use of the coating composition containing a large amount of the surfactant results in a coating film having low strength and adhesion, and therefore the method (4) is not still satisfactory. The conventional method (5) has a drawback that a coating film concurrently having high anti-fogging property and film strength can not be obtained due to the reason that the anti-fogging treatment of polyester film must be carried out in a short curing time. That is, the lower are the concentration of crosslinkable functional group in the hydrophilic polymer and the concentration of the crosslinking agent, the higher the anti-fogging performance of the resulting coating film is. However, in this case, the resulting coating film has

not a fully crosslinked structure due to the short curing time, and hence the coating film is very poor in the strength and adhesion and can not at all be practically used. On the contrary, when the hydrophilic polymer having crosslinkable functional groups in a high concentration is used in order to obtain a coating film having a high strength, the resulting coating film is very poor in the anti-fogging property, and moreover when a surfactant is contained in the coating composition in order to develop an anti-fogging property, the resulting coating film has initially a high anti-fogging property due to the surfactant bled to surface of the coating film, but when the coating film surface is immersed in water, the surfactant bled to the coating film surface is flowed away, and further a surfactant contained in the interior of the coating film can not be bled to the film surface due to the high concentration of the crosslinking agent and hence the anti-fogging property of the coating film is low. The conventional method (6) has a drawback that, although the curing time is short, the curing reaction is apt to proceed rapidly due to the reason that the radical curing reaction is a chain reaction, and therefore the resulting coating film has a very high crosslink density and is poor in the anti-fogging property.

As described above, a satisfactory anti-fogging method for various transparent materials has not yet been found out.

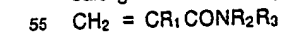
The object of the present invention is to provide an anti-fogging resin film-forming composition not only having a high initial anti-fogging property, but also having a highly durable anti-fogging property and having an excellent coating property.

The inventors have already proposed, in Japanese Patent Application No. 58-74,959, a block copolymer consisting of a hydrophilic polymer segment and a hydrophobic polymer segment, as an anti-fogging composition having a durable wettability and further having a high adhesion to the surface of a matrix to be coated. The inventors have further made various investigations and have found out that, when a block copolymer consisting of a hydrophilic polymer segment and a hydrophobic polymer segment or a graft copolymer consisting of a hydrophilic polymer segment and a hydrophobic polymer segment is mixed with a surfactant, the resulting coating composition can form a coating film on a transparent material, which coating film has such a highly durable wettability that can never been anticipated by the prior technic, and further has a high adhesion to the material surface and a high mar resistance, and can eliminate the drawbacks of conventional technics. As the result, the present invention has been accomplished.

That is, the first aspect of the present invention lies in an anti-fogging resin film-forming composition, comprising at least one copolymer selected from block copolymers and graft copolymers, and a surfactant, each of which block copolymer and which graft copolymer consists of a hydrophilic polymer segment and a hydrophobic polymer segment.

The inventors have further investigated and found out that, when an anti-fogging resin film forming composition is formed of a block copolymer and a surfactant, which block copolymer consists of a hydrophilic polymer segment containing a specifically limited crosslinkable functional group, and a hydrophobic polymer segment containing a specifically limited crosslinkable functional group, the weight ratio of the hydrophilic polymer segment to the hydrophobic polymer segment being a specifically limited ratio, a coating film resulted from the coating composition and formed on a matrix has a high adhesion to the matrix surface even under an environment, which causes a thermal history in the coating film, and further has high strength and high anti-fogging property.

That is, the second aspect of the present invention lies in an anti-fogging resin film-forming composition, comprising a block copolymer, which consists of a hydrophilic polymer segment and a hydrophobic polymer segment, and a surfactant, which hydrophilic polymer segment is formed of 1-40% by weight of at least one of N-substituted or non-substituted (meth)acrylamide-type compounds (in the specification and claims, the term "(meth)acryl" means acryl and methacryl) represented by the following general formula (I) or (II), 1-20% by weight of at least one monomer selected from the group (referred to as Group A) consisting of monomers having a crosslinkable functional group of any one of glycidyl group, N-methylol group, N-methylether group, carboxyl group and acid anhydride, and 40-98% by weight of at least one of hydrophilic monomers copolymerizable with the above described (meth)acrylamide-type compound and the monomer of the above described Group A, and which hydrophobic polymer segment is formed of 1-40% by weight of at least one monomer selected from the monomers of Group A and 60-99% by weight of at least one hydrophobic monomer copolymerizable with the monomer of Group A, the weight ratio of the hydrophilic polymer segment to the hydrophobic polymer segment being within the range of 50/50-95/5, said general formula (I) being



wherein R_1 and R_2 represent hydrogen atoms or methyl groups; and R_3 represents hydrogen atom, methyl group, ethyl group, n-propyl group, isopropyl group, N,N-dimethylaminopropyl group or $-\text{C}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3$, and said general formula (II) being



wherein R_1 represents hydrogen atom or methyl group; and A represents $-(\text{CH}_2)_n-$ (wherein n is a positive integer of 4 or 5) or $-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$.

Further, the inventors have found that, when an anti-fogging resin film-forming composition is formed of a mixture of a block or graft copolymer, which consists of a hydrophilic polymer segment and a hydrophobic polymer segment and has a self-crosslinking property, with a surfactant, a coating film formed from the coating composition has concurrently high anti-fogging property and strength. Particularly, a coating film having both the excellent properties can be formed on a polyester film from the coating composition in a short curing time.

That is, the third aspect of the present invention lies in an anti-fogging resin film-forming composition, comprising a block or graft copolymer and a surfactant, which block or graft copolymer consists of a hydrophilic polymer segment formed of 6-25% by weight of a monomer of glycidyl (meth)acrylate or N-methylolacrylamide, 43-90% by weight of hydroxyalkyl (meth)acrylate, and 4-32% by weight of a monomer selected from the group consisting of acrylamide, N-monomethylacrylamide, N,N-dimethylacrylamide, N-acryloylmorpholine and N-vinylpyrrolidone, and a hydrophobic polymer segment formed of 50-85% by weight of lower alkyl (meth)acrylate and 15-50% by weight of (meth)acrylic acid.

Firstly, an explanation will be made with respect to the block copolymer and the graft copolymer, each consisting of a hydrophilic polymer segment and a hydrophobic polymer segment, to be used in the anti-fogging resin film-forming composition of the first aspect of the present invention.

As the vinyl monomer for forming a hydrophilic polymer segment, which constitutes one of the molecular chains of the block copolymer or the graft copolymer to be used in the first aspect of the present invention, there can be used, for example, radically polymerizable unsaturated carboxylic acids, such as (meth)acrylic acid, itaconic acid, crotonic acid and the like, and their alkali metal salts, ammonium salts and organic amine salts; radically polymerizable unsaturated monomers having a sulfonic acid group, such as styrenesulfonic acid, sulfopropyl (meth)acrylate, sulfopropyl itaconate and the like, and their alkali metal salts, ammonium salts and organic amine salts; quaternary ammonium salts derived from (meth)acrylic acid, such as methacryloyloxyethyltrimethylammonium chloride, 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride and the like; methacrylic acid esters of alcohol having a tertiary amino group, such as methacrylic acid diethyl amino ester and the like, and their quaternary ammonium salts; radically polymerizable unsaturated monomers having an amide group, such as (meth)acrylamide, dimethylacrylamide and the like; quaternary ammonium salts derived from an amido-amine obtained from methacrylic acid and diamine; hydroxy esters of (meth)acrylic acid, such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate and the like; polyethylene glycol esters or polypropylene glycol esters of (meth)acrylic acid, such as diethylene glycol (meth)acrylate, triethylene glycol (meth)acrylate, dipropylene glycol (meth)acrylate and the like; polyhydric alcohol esters of (meth)acrylic acid, such as (meth)acrylic acid monoglyceride and the like; phosphoric acid salts of (meth)acrylic acid, such as mono-(2-hydroxyethyl acrylate) acid phosphate and the like; betaine-type radically polymerizable unsaturated monomers, such as N-(3-sulfopropyl)-N-methacryloyloxyethyl-N,N-dimethylammonium betaine, N-(3-sulfopropyl)-N-methacryloylamidopropyl-N,N-dimethylammonium betaine, 1-(3-sulfopropyl)-2-vinylpyridinium betaine and the like; vinylpyridine and its salts; vinylpyrrolidone and the like. These vinyl monomers can be used in combination with other vinyl monomers, the amount of which is such that the latter vinyl monomer does not deteriorate the hydrophilic property of the resulting hydrophilic polymer.

The vinyl monomer, which forms a hydrophobic polymer segment constituting the other molecular chain of the block copolymer or the graft copolymer to be used in the first aspect of the present invention, should be properly selected from the viewpoint of the strength and adhesion of the coating film to be formed on an object transparent matrix. Particularly, when the transparent matrix is a polymer material, the vinyl monomer should be selected by taking into consideration the compatibility of the vinyl monomer with the base resin of the polymer material to be coated. These vinyl monomers include, for example, (meth)acrylates, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, glycidyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate and the like; aromatic vinyl monomers, such as styrene, vinyltoluene, α -methylstyrene and the like; vinyl carboxylates, such as vinyl formate, vinyl acetate, vinyl propionate, vinyl stearate and the like; butadiene; vinyl chloride; vinylidene chloride; (meth)acrylonitrile; (meth)allyl glycidyl ether; and the like.

The block copolymer and the graft copolymer, each consisting of a hydrophilic polymer segment and a hydrophobic polymer segment, of the present invention can be produced by various conventional polymerization processes, for example, by the free-radical polymerization process, the cationic ring-opening polymerization process, anionic living polymerization process, and cationic living polymerization process.

However, in the present invention, a block copolymer or a graft copolymer is advantageously produced through a free-radical polymerization process with the use of a polymeric peroxide, a polyazo compound or a radically copolymerizable group-containing peroxide as a polymerization initiator in view of the easiness of the commercial production of the copolymer and the various performances of the resulting copolymer. In this case, as the free-radical polymerization initiator, there can be used a commonly known compound having at least 2 peroxy bonds or azo bonds in one molecule, or a compound concurrently having a radically copolymerizable group and a peroxy bond in one molecule, and the block copolymer or the graft copolymer can be easily obtained by an ordinary bulk polymerization process, suspension polymerization process, solution polymerization process or emulsion polymerization process.

A typical method for the production of the block copolymer of the present invention with the use of a polymeric peroxide as a polymerization initiator is as follows. When a hydrophilic polymer-formable vinyl monomer is first polymerized in the presence of a polymeric peroxide, a hydrophilic vinyl polymer containing peroxy bonds introduced into its polymer chain is obtained, and thereafter when the peroxy bond-containing hydrophilic vinyl polymer is polymerized together with a hydrophobic polymer-formable vinyl monomer, the peroxy bond-containing hydrophilic vinyl polymer is cleaved at the peroxy bonds contained therein, and an aimed block copolymer is efficiently obtained. While, a typical method for producing the graft copolymer of the present invention with the use of a radically copolymerizable group-containing peroxide as a polymerization initiator is as follows. When a vinyl monomer, which can be polymerized into a hydrophilic polymer in the presence of an ordinary free-radical polymerization initiator, is first copolymerized in the presence of a radically copolymerizable group-containing peroxide under a condition that the peroxy bonds in the radically copolymerizable group-containing peroxide are not cleaved, a peroxy bond-containing hydrophilic copolymer can be obtained, and thereafter when the resulting peroxy bond-containing hydrophilic copolymer is polymerized together with a hydrophobic polymer-formable vinyl monomer under a condition that the peroxy bonds are cleaved, the peroxy bond-containing hydrophilic copolymer is cleaved at the peroxy bonds contained therein, and an aimed graft copolymer is efficiently obtained. In the block copolymer and the graft copolymer obtained by the above described methods, the molecular weights of the hydrophilic polymer segment and hydrophobic polymer segment can be freely adjusted.

The weight ratio of the hydrophilic polymer segment to the hydrophobic polymer segment in the block copolymer and in the graft copolymer of the first aspect of the present invention is preferably 1/19-19/1, and more preferably 1/9-9/1. A block copolymer or a graft copolymer containing less than 5% by weight of a hydrophilic polymer segment is poor in the compatibility with the surfactant to be used in the present invention, and has such a risk that the surfactant is easily separated out from the resulting coating film and the durability of the anti-fogging property of the coating film is deteriorated. While, a block copolymer or a graft copolymer containing less than 5% by weight of a hydrophobic polymer segment has such a risk that the resulting coating film is poor in the adhesion with the surface of a matrix to be modified and further is poor in the water resistance and in the mechanical strength. Therefore, the block copolymer or graft copolymer containing less than 5% by weight of a hydrophilic polymer segment or a hydrophobic polymer segment cannot be used satisfactorily for the practical purpose.

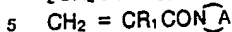
Hereinafter, an explanation will be made with respect to the second aspect of the present invention.

In the second aspect of the present invention, an anti-fogging resin film-forming composition is formed of a block copolymer consisting of a hydrophilic polymer segment and a hydrophobic polymer segment, each containing a specifically limited crosslinkable functional group, in combination with a surfactant, whereby a coating film having a high adhesion to the surface of a matrix even under an environment, which causes a thermal history in the coating film, and further having high strength and anti-fogging property is obtained.

The block copolymer to be used in the second aspect of the present invention consists of a hydrophilic polymer segment and a hydrophobic polymer segment, which hydrophilic polymer segment is formed of 1-40% by weight of at least one of N-substituted or non-substituted (meth)acrylamide-type compounds represented by the following general formula (I) or (II), 1-20% by weight of at least one monomer selected from the group (referred to as Group A) consisting of monomers having a crosslinkable functional group of any one of glycidol group, N-methylol group, N-methylether group, carboxyl group and acid anhydride, and 40-98% by weight of at least one of hydrophilic monomers copolymerizable with the above described (meth)acrylamide-type compound and the monomer of the above described group A, and which hydrophobic polymer segment is formed of 1-40% by weight of at least one monomer selected from the monomers of Group A and 60-99% by weight of at least one hydrophobic monomer copolymerizable with the monomer of Group A, the weight ratio of the hydrophilic polymer segment to the hydrophobic polymer segment being within the range of 50/50-95/5, said general formula (I) being



wherein R_1 and R_2 represent hydrogen atoms or methyl groups; and R_3 represents hydrogen atom, methyl group, ethyl group, n-propyl group, isopropyl group, N,N-dimethylaminopropyl group or $-\text{C}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3$, and said general formula (II) being



wherein R_1 represents hydrogen atom or methyl group; and A represents $-(\text{CH}_2)_n-$ (wherein n is a positive integer of 4 or 5) or $(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$.

As the N-substituted or non-substituted (meth)acrylamide-type compound to be introduced into the hydrophilic polymer segment constituting one of the molecular chains of the block copolymer to be used in the second aspect of the present invention, there can be used (meth)acrylamide, N-methyl(meth)-acrylamide, N,N-dimethyl(meth)acrylamide, N-ethyl(meth)acrylamide, N,N-diethyl(meth)acrylamide, N-n-propyl(meth)acrylamide, N-isopropyl(meth)acrylamide, N,N-dimethylaminopropyl(meth)acrylamide, diacetone(meth)acrylamide, N-(meth)acryloylpyrrolidine, N-(meth)acryloylpiperidine, N-(meth)-acryloylmorpholine and the like.

It is necessary that the monomer units of the above described (meth)acrylamide-type compound are contained in the hydrophilic polymer segment in an amount of within the range of 1-40% by weight. When the amount is less than 1% by weight, the resulting coating film is poor in the durability and in the adhesion after thermal history is caused in the film, and when the amount is more than 40% by weight, the resulting coating film is poor in the strength.

As the monomer of Group A, which has a crosslinkable functional group, there can be used glycidyl (meth)acrylate, N-methylol(meth)acrylamide, N-methoxymethylol(meth)acrylamide, N-butoxymethylol(meth)acrylamide, (meth)acrylic acid, crotonic acid, itaconic acid, itaconic acid half ester, maleic acid, maleic acid half ester, itaconic anhydride, maleic anhydride and the like.

It is necessary that the monomer units of the above described monomer of Group A are contained in the hydrophilic polymer segment in an amount of 1-20% by weight. When the amount of the monomer units of the monomer of Group A is less than 1% by weight, the resulting coating film is unsatisfactory in the strength, and when the amount of the monomer units of the monomer of Group A is more than 20% by weight, the resulting coating film has an extremely high degree of crosslinking and is poor in the anti-fogging property.

As the hydrophilic monomer, which is copolymerizable with the above described (meth)acrylamide-type compound and the above described monomer of Group A having a crosslinkable functional group, there can be advantageously used monomers, which does not at all cause or does not substantially cause a crosslinking reaction with the functional group in the monomer of Group A. These monomers include radically polymerizable unsaturated carboxylic acids, such as (meth)acrylic acid, itaconic acid, crotonic acid and the like, and their alkali metal salt, ammonium salt and organic amine salt; radically polymerizable unsaturated monomers having a sulfonic acid group, such as styrene sulfonic acid, sulfopropyl (meth)acrylate and the like, and their alkali metal salt, ammonium salt and organic amine salt; quaternary ammonium salts derived from (meth)acrylic acid, such as methacryloyloxyethyltrimethylammonium chloride, 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride and the like; hydroxy esters of (meth)acrylic acid, such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate and the like; polyethylene glycol esters or polypropylene glycol esters of (meth)acrylic acid, such as diethylene glycol (meth)acrylate, triethylene glycol (meth)acrylate, dipropylene glycol (meth)acrylate and the like; polyhydric alcohol esters of (meth)acrylic acid, such as mono(2-hydroxyethyl)oglyceride and the like; phosphoric acid salts of (meth)acrylic acid, such as mono(2-hydroxyethyl) methacrylate) acid phosphate and the like; betaine-type radically polymerizable unsaturated monomers, such as N-(3-sulfopropyl)-N-methacryloyloxyethyl-N,N-dimethylammonium betaine, 1-(3-sulfopropyl)-2-vinylpyridinium betaine and the like; vinylpyridine and its salts; vinylpyrrolidone; and the like.

It is necessary that the hydrophilic polymer segment of the block copolymer to be used in the second aspect of the present invention contains 40-98% by weight of monomer units of at least one of hydrophilic monomers, which are copolymerizable with the above described (meth)acrylamide-type monomer and the above described monomer of Group A.

It is indispensable that the hydrophobic polymer segment, which constitutes the other polymer chain of the block copolymer of the second aspect of the present invention, is formed of 1-40% by weight of a monomer of Group A and 60-99% by weight of a hydrophobic monomer copolymerizable with the monomer of Group A.

In this case, it is preferable that a monomer which has a high reactivity with the functional group introduced into the hydrophilic polymer segment, is selected from the monomers of Group A. For example, when a glycidyl group is contained in the hydrophilic polymer segment, carboxylic acid group or acid

anhydride is preferably introduced into the hydrophobic polymer segment. Conversely, when carboxylic acid group or acid anhydride is contained in the hydrophilic polymer segment, it is preferable that glycidyl group is introduced in the hydrophobic polymer segment. When a functional group having a high self-crosslinking property, such as N-methylol group or N-methylolether group, is contained in the hydrophilic polymer segment, either N-methylol group or N-methylolether group may be introduced into the hydrophobic polymer segment, or carboxylic acid group or acid anhydride may be introduced into the hydrophobic polymer segment.

When less than 1% by weight of the monomer units of a monomer of the above described Group A is contained in the hydrophobic polymer segment, the resulting coating film is short in the strength, and when more than 40% by weight of the monomer units of a monomer of the above described Group A is contained in the hydrophobic polymer segment, the resulting coating film is poor in the adhesion to the surface of a matrix to be coated.

The hydrophobic monomer copolymerizable with the monomer of the above described Group A is properly selected by taking into consideration the adhesion of the resulting coating film with the matrix to be coated. As the hydrophobic monomer copolymerizable with the monomer of Group A, there can be used (meth)acrylates, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and the like; aromatic vinyl monomers, such as styrene, vinyltoluene, α -methylstyrene and the like; vinyl carboxylates, such as vinyl formate, vinyl acetate, vinyl propionate and the like; butadiene; vinyl chloride, vinylidene chloride; (meth)acrylonitrile; allyl glycidyl ether; and the like.

In the block copolymer to be used in the anti-fogging resin film-forming composition of the second aspect of the present invention, the hydrophilic polymer segment and the hydrophobic polymer segment have a composition corresponding to the above described mixing ratio of the monomers.

In the block copolymer constituting the anti-fogging resin film-forming composition of the second aspect of the present invention, it is necessary that the weight ratio of the hydrophilic polymer segment to the hydrophobic polymer segment is within the range of 50/50-95/5. When the weight ratio of the hydrophilic polymer segment to the hydrophobic segment is less than 50/50, the affinity of the resulting coating film to the surfactant is poor and the surfactant is easily separated out from the coating film, and the coating film is poor in the durability of anti-fogging property. When the weight ratio of the hydrophobic polymer segment to the hydrophilic polymer segment is less than 5/95, not only the adhesion of the resulting coating film to the surface of the matrix to be coated is poor, but also the coating film is poor in the strength, and hence a coating composition containing a block copolymer having a weight ratio of the hydrophilic polymer segment to the hydrophobic polymer segment outside the above described range of 50/50-95/5 can not be practically used.

The third aspect of the present invention will be explained hereinafter.

In the third aspect of the present invention, an anti-fogging resin film-forming composition is formed of a mixture of a block or graft copolymer, which consists of a hydrophilic polymer segment and a hydrophobic polymer segment and has a self-crosslinking property, with a surfactant, whereby a coating film having both excellent anti-fogging property and high strength is obtained. Particularly, this coating composition has such a merit that a coating film having both the excellent properties can be formed on a polyester film in a short curing time.

The block or graft copolymer having a self-crosslinking property to be used in the third aspect of the present invention consists of a hydrophilic polymer segment and a hydrophobic polymer segment, which hydrophilic polymer segment is formed of 6-25% by weight of a monomer of glycidyl (meth)acrylate or N-methylolacrylamide, 43-90% by weight of hydroxyalkyl (meth)acrylate, and 4-32% by weight of a monomer selected from the group consisting of acrylamide, N-monomethylacrylamide, N,N-dimethylacrylamide, N-acryloylmorpholine and N-vinylpyrrolidone, and which hydrophobic polymer segment is formed of 50-85% by weight of lower alkyl (meth)acrylate and 15-50% by weight of (meth)acrylic acid.

An explanation will be made with respect to the monomers constituting the hydrophilic polymer segment of the block or graft copolymer in the third aspect of the present invention.

Glycidyl (meth)acrylate or N-methylolacrylamide is used as follows. In the case where an anti-fogging resin film-forming composition is applied on a polyester film surface and the composition is heated and cured, when the curing temperature is about 80-140°C, N-methylolacrylamide is advantageously used, and when the curing temperature is about 120-230°C, glycidyl (meth)acrylate is advantageously used. This glycidyl (meth)acrylate or N-methylolacrylamide is used in an amount of 6-25% by weight based on the total amount of a monomer mixture for forming the hydrophilic polymer segment.

As the hydroxyalkyl (meth)acrylate, there are used hydroxy-lower alkyl (meth)acrylates and the like, and hydroxyethyl (meth)acrylate is preferably used.

This hydroxyalkyl (meth)acrylate is used in an amount of 43-90% by weight based on the total amount of a monomer mixture for forming the hydrophilic polymer segment.

As the monomer selected from the group consisting of acrylamide, N-monomethylacrylamide, N,N-dimethylacrylamide, N-acryloylmorpholine and N-vinylpyrrolidone, there are preferably used N-monomethylacrylamide, N,N-dimethylacrylamide and N-acryloylmorpholine. This monomer is used in an amount of 4-32% by weight based on the total amount of a monomer mixture for forming the hydrophilic polymer segment.

An explanation will be made with respect to the monomers constituting the hydrophobic polymer segment of the block or graft copolymer to be used in the third aspect of the present invention.

As the lower alkyl (meth)acrylate, there can be used methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate and the like. Among them, methyl (meth)acrylate is preferably used. This lower alkyl (meth)acrylate is used in an amount of 50-85% by weight based on the total amount of a monomer mixture for forming the hydrophobic polymer segment.

(Meth)acrylic acid is used in an amount of 15-50% by weight based on the total amount of a monomer mixture for forming the hydrophobic polymer segment.

The above described amount ratio of monomers, which are used for the formation of the hydrophilic polymer segment or for the formation of the hydrophobic polymer segment, should be determined from both the anti-fogging property and the strength of the coating film to be formed on the matrices, such as polyester film and the like, and when the amount ratios of the monomers are outside the above described ranges, a coating film having both the excellent anti-fogging property and high strength can not be obtained.

Since the block or graft copolymer to be used in the third aspect of the present invention has a self-crosslinking property, it is preferable to select monomers such that the functional group to be introduced into the hydrophobic polymer segment has a high reactivity with the functional group introduced into the hydrophilic polymer segment. For example, when glycidyl group is contained in the hydrophilic polymer segment, it is preferable to introduce carboxylic acid group or sulfonic acid group into the hydrophobic polymer segment. Reversely, when carboxylic acid group or sulfonic acid group is contained in the hydrophilic polymer segment, it is preferable to introduce glycidyl group into the hydrophobic polymer segment. Further, when a functional group, such as N-methylol group or the like, having a high self-crosslinking property is contained in the hydrophilic polymer segment, N-methyl group, carboxylic acid group or sulfonic acid group may be contained in the hydrophobic polymer segment.

In the above obtained block copolymer or graft copolymer, the molecular weights of the hydrophilic polymer segment and the hydrophobic polymer segment can be freely adjusted. Further, the graft copolymer may be either a graft copolymer, wherein the backbone is formed of a hydrophilic polymer segment and the superstrate is formed of a hydrophobic polymer segment, or a graft copolymer, wherein the backbone is formed of a hydrophobic polymer segment and the superstrate is formed of a hydrophilic polymer segment. Moreover, in the present invention, a combination use of the block copolymer and the graft copolymer can attain the same effect as that attained by the use of the block copolymer or the graft copolymer alone.

In the block copolymer or graft copolymer to be used in the third aspect of the present invention, the weight ratio of hydrophilic polymer segment/hydrophobic polymer segment is preferably within the range of 1/9-9/1, more preferably within the range of 1/5-5/1. When the amount of the hydrophilic polymer segment is less than 10% by weight, the resulting coating film is poor in the anti-fogging property and further the block copolymer is poor in the compatibility with surfactant, and there is a risk that the surfactant is easily separated out from the resulting coating film and the durability of the coating film is deteriorated. While, when the amount of the hydrophobic polymer segment is less than 10% by weight, there is a risk that the resulting coating film is poor in the adhesion to the matrix surface to be modified, and further the resulting coating film is apt to be poor in the water resistance and mechanical strength. Therefore, a block copolymer and graft copolymer containing less than 10% by weight of hydrophilic polymer segment or hydrophobic polymer segment can not be practically used.

In the present invention, there can be used at least one surfactant selected from ordinarily used surfactants, that is, nonionic surfactant, anionic surfactant, cationic surfactant and amphoteric surfactant. Particularly, nonionic surfactant and anionic surfactant are preferably used in view of the durability of the effect. Further, a combination system of nonionic surfactant and anionic surfactant is more preferably used.

As the nonionic surfactant, there can be used, for example, polyoxyethylene higher alcohol ethers, such as polyoxyethylene stearyl ether, polyoxyethylene lauryl ether, polyoxyethylene oleyl ether and the like; polyoxyethylene alkylaryl ethers, such as polyoxyethyleneoctylphenol, polyoxyethylenenonylphenol and the like; polyoxyethylene acyl esters, such as polyethylene glycol monostearate and the like; polypropylene

glycol ethylene oxide additives; polyoxyethylenesorbitan fatty acid esters, such as polyoxyethylenesorbitan monostearate and the like; phosphates, such as alkyl phosphate, polyoxyethylenealkyl ether phosphate and the like; sugar esters; cellulose ethers; and the like.

As the anionic surfactant, there can be used, for example, fatty acid metal salts, such as sodium oleate, potassium oleate and the like; higher alcohol sulfuric acid esters, such as sodium lauryl sulfate, ammonium lauryl sulfate and the like; alkylbenzene sulfonates and alkylnaphthalenesulfonates, such as sodium dodecylbenzenesulfonate, sodium alkylnaphthalenesulfonate and the like; naphthalenesulfonic acid-formaldehyde condensate; dialkyl sulfosuccinate; dialkyl phosphate; polyoxyethylene sulfates, such as sodium polyoxyethylene alkylether sulfate, sodium polyoxyethylene alkylphenylether sulfate and the like; and the like.

As the cationic surfactant, there can be used, for example, ethanolamines; amine salts, such as laurylamine acetate, triethanolaminemonostearate formic acid salt, stearylamine-ethyl-diethylamine acetic acid salt and the like; quaternary ammonium salts, such as lauryltrimethylammonium chloride, stearyltrimethylammonium chloride, dialauryldimethylammonium chloride, distearyldimethylammonium chloride, lauryldimethylbenzylammonium chloride, stearyldimethylbenzylammonium chloride and the like; and the like.

As the amphoteric surfactant, there can be used aliphatic-type amphoteric surfactants, such as dimethylalkyllauryl betaine, dimethylalkylstearyl betaine and the like; sulfonic acid-type amphoteric surfactants, dimethylalkyl sulfobetaine and the like; alkylglycine; and the like.

In the film-forming composition in the present invention, 0.1-20 parts by weight of a surfactant is preferably used based on 100 parts by weight of the block copolymer or the graft copolymer. When the amount of the surfactant is less than 0.1 part by weight, it is difficult to obtain a coating film having a high durability of anti-fogging property aimed in the present invention. While, when the amount of the surfactant is more than 20 parts by weight, there is a risk that the resulting coating film is poor in the water resistance and mechanical strength.

In the present invention, the surfactant can be mixed with the block copolymer or graft copolymer in the following manner. That is, a block copolymer or graft copolymer is first dissolved or dispersed in organic solvent, in a mixture of water and organic solvent or in water, and then a surfactant may be directly added to the solution or dispersion of the copolymer. Alternatively, a surfactant is mixed with vinyl monomers, which are to be formed into a block copolymer or graft copolymer, at the production of the block copolymer or graft copolymer.

In general, the film-forming composition of the present invention is applied on the surface of a transparent matrix or on a mirror-surfaced matrix, and the applied composition is dried at room temperature or under heating to form a coating film on the matrix. As the application method of the film-forming composition, there can be used ordinary application methods, that is, roll coat method, spray method, immersion method, brushing method, spin coat method and the like. As the solvent to be used in this application, there can be used water; alcohols, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, diacetone alcohol and the like; alcohol ethers, such as methyl cellosolve, ethyl cellosolve, butyl cellosolve, methylcarbitol, ethylcarbitol, butylcarbitol and the like; ketones, such as methyl ethyl ketone, methyl isobutyl ketone and the like; esters, such as methyl acetate, ethyl acetate, butyl acetate and the like; aromatic hydrocarbons, such as benzene, toluene, xylene and the like; and amides, such as formamide, dimethylformamide and the like. Among them, alcohols, alcohol ethers and mixed solvents of alcohol and alcohol ether are particularly preferable solvents.

The anti-fogging resin film-forming composition of the present invention can be used in combination with a commonly used curing agent and resin in order to enhance the strength in the resulting coating film. For example, there can be used various amino resins, such as alkoxymethylolmelamine-formamide resin, alkylated benzoguanamine resin, urea resin and the like; isocyanate group-containing resins, such as adduct-type polyisocyanate obtained by reacting tolylene diisocyanate with trimethylolpropane, biuret-type polyisocyanate obtained by reacting trimers of hexamethylene diisocyanate, various blocked isocyanates and the like; bisphenol A-type epoxy resin; bisphenol F-type epoxy resin; polyepoxy compounds, such as trimethylolpropane polyglycidyl ether, neopentylglycol diglycidyl ether and the like; compounds having at least 2 hydroxyl groups, such as polyethylene glycol, polypropylene glycol and the like; compounds having at least 2 carboxyl groups, such as dodecanedioic acid and the like; and the like. The use amount of the curing agent is preferably 0-30% by weight based on the amount of the block copolymer or graft copolymer. When the amount exceeds 30% by weight, the curing agent influences adversely the effect of the present invention.

Further, the anti-fogging resin film-forming composition can be occasionally mixed with commonly known various additives, such as ultraviolet absorbing agent, leveling agent, various curing catalysts,

antioxidant and the like.

The reason why the anti-fogging resin film-forming composition of the present invention has excellent coating performance is not clear, but is probably as follows. When a block copolymer or graft copolymer is mixed with a surfactant, the hydrophilic polymer segment in the block copolymer or graft copolymer and the surfactant are attracted with each other, and the surfactant is homogeneously dispersed into the block copolymer or into the graft copolymer. Therefore, in the coating film formed from this homogeneous dispersion, the hydrophilic polymer segment in the block copolymer or graft copolymer acts as an anchor of the surfactant to fix tightly the surfactant in the coating film. When water is adhered on the coating film surface, the surfactant is gradually bled out on the coating film surface from the interior of the coating film, and the anti-fogging performance and the durability of the anti-fogging property of the coating film are remarkably improved due to the synergistic effect of the hydrophilic polymer segment in the block or graft copolymer and the surfactant bled out from the interior of the coating film. While, the hydrophobic polymer segment in the block copolymer or graft copolymer is tightly stuck to the matrix surface to form a coating film having high water resistance, corrosion resistance and high strength.

The anti-fogging resin film-forming composition of the present invention results in a coating film having everlasting excellent anti-fogging property for the matrix surface. Further, the resulting coating film has excellent adhesion to transparent materials, such as various plastic materials, glass, transparent ceramics and the like, and to the surface of various mirror materials, and further has excellent water resistance and mechanical strength. Therefore, the anti-fogging resin film-forming composition of the present invention has completely solved the problems in the conventional various anti-fogging paints.

Accordingly, the anti-fogging resin film-forming composition of the present invention is remarkably effective in the use as anti-fogging agent for various plastic molded materials, mirror for dressing table in toilet room, mirror in bathroom, window glass in building and automobile, curve mirror, light reflector, agricultural film, packing film for foods and the like.

The present invention will be explained in more detail referring to the following examples, comparative examples and reference examples. In the examples, "parts" and "%" are by weight unless otherwise indicated.

Reference example 1

(Production of a hydrophilic and hydrophobic block copolymer)

(1-1) Production of a peroxy bond-containing polymer:

Into a reactor equipped with a thermometer, a stirrer and a reflux cooler was charged 90 parts of methyl cellosolve, and while introducing nitrogen gas into the reactor and heating the reaction system at 70°C, a mixed solution (I) consisting of

methyl cellosolve : 30 parts

2-hydroxyethyl methacrylate : 30 parts

and

$$\text{---} \left[\text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{(CH}_2\text{)}_4 \text{CO} \end{array} \begin{array}{c} \text{O} \\ \parallel \\ \text{(C}_2\text{H}_4\text{O)}_3 \end{array} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \begin{array}{c} \text{O} \\ \parallel \\ \text{(CH}_2\text{)}_4 \text{COO} \end{array} \right]_{5.5} \text{---}$$
 : 6 parts

was charged into the reactor in 2 hours, and further a polymerization reaction was effected for 2 hours. The resulting solution was a transparent solution containing 23.1% of a peroxy bond-containing polymer and having a viscosity of 1.8 poises at 25°C.

(1-2) Production of a block copolymer:

In a reactor equipped with a thermometer, a stirrer and a reflux cooler, a mixed solution (II) consisting of 100 parts of the methyl cellosolve solution of peroxybond-containing polymer obtained in the above described Step 1-1 and 20 parts of methylmethacrylate was heated at 70°C for 6 hours while introducing nitrogen gas into the reactor, to effect a block copolymerization reaction and to obtain a transparent solution containing 42.8% of a block copolymer and having a viscosity of 5.5 poises at 25°C.

10 Reference example 2

(Production of a hydrophilic and hydrophobic block copolymer)

15 (2-1) Production of a peroxy bond-containing polymer:

Into a reactor equipped with a thermometer, a stirrer and a reflux cooler was charged 90 parts of ethyl cellosolve, and while introducing nitrogen gas into the reactor and heating the reaction system at 70°C, a mixed solution (III) consisting of

methyl cellosolve	: 60 parts
2-hydroxyethyl methacrylate	: 55 parts
N-methylolacrylamide	: 5 parts
and	
$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ -\text{C}(\text{CH}_2)_5\text{CH}(\text{CH}_2)_6\text{COO}- \\ \\ \text{CH}_2\text{CH}_3 \end{array}$: 9 parts

was charged into the reactor in 3 hours, and further a polymerization reaction was effected for 3 hours. The resulting solution was a transparent solution containing 31.5% of a peroxy bond-containing polymer and having a viscosity of 7.5 poises at 25°C.

20 (2-2) Production of a block copolymer:

In a reactor equipped with a thermometer, a stirrer and a reflux cooler, a mixed solution (IV) consisting of 100 parts of the ethyl cellosolve solution of peroxy bond-containing polymer obtained in the above described Step 2-1, 8 parts of methyl methacrylate and 1 part of acrylic acid was heated at 70°C for 6 hours and further at 80°C for 2 hours while introducing nitrogen gas into the reactor, to effected a block copolymerization reaction and to obtain a transparent solution containing 40.3% of a block copolymer and having a viscosity of 7.3 poises at 25°C.

50 Reference example 3

(Production of a hydrophilic and hydrophobic graft copolymer)

55 (3-1) Production of a peroxy bond-containing polymer:

Into a reactor equipped with a thermometer, a stirrer and a reflux cooler was charged 150 parts of methyl cellosolve, and while introducing nitrogen gas into the reactor and heating the reaction system at 85° C, a mixed solution (V), which had previously been produced by dissolving 1.5 parts of t-butylperoxy 2-ethylhexanoate (trademark: Perbutyl O, sold by Nippon Oil and Fats Co., Ltd., 10 hour half-value period temperature: 72° C) and 6 parts of t-butylperoxy methacryloyloxyethyl carbonate used as radically copolymerizable organic peroxide in a mixture of 280 parts of 2-hydroxyethyl methacrylate, 20 parts of glycidyl methacrylate and 300 parts of methyl cellosolve, was charged into the reactor in 2 hours, and further a polymerization reaction was effected for 7 hours. The resulting solution was a transparent solution containing 40.1% of a peroxy bond-containing polymer and having a viscosity of 5.7 poises at 25° C.

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(3-2) Production of a graft copolymer:

Into a reactor equipped with a thermometer, a stirrer and a reflux cooler was charged 100 parts of the methyl cellosolve solution obtained in the above described Step 3-1 and containing the peroxy bond-containing polymer, and while introducing nitrogen gas into the reactor and heating the reaction system at 110° C, a mixed solution (VI) consisting of

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methyl methacrylate :	8 parts
methacrylic acid :	2 parts
and	
methyl cellosolve :	50 parts

was charged into the reactor in 2 hours, and further a graft polymerization reaction was effected for 7 hours. The resulting solution was a transparent solution containing 31% of a graft copolymer and having a viscosity of 3.5 poises at 25° C.

30 Reference example 4

(Production of a hydrophilic and hydrophobic graft copolymer)

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(4-1) Production of a peroxy bond-containing polymer:

Into a reactor equipped with a thermometer, a stirrer and a reflux cooler were charged 90 parts of isopropanol and 60 parts of water, and while introducing nitrogen gas into the reactor and heating the reaction system at 80° C, a mixed solution (VII), which had previously been prepared by dissolving 3.0 parts of t-butylperoxy octanoate and 6.0 parts of a radically copolymerizable organic peroxide of t-butylperoxy methacryloyloxyethyl carbonate in a mixture of 50 parts of 2-hydroxy-3-methacryloyloxypropyl-trimethylammonium chloride (trademark: Blemmer QA, sold by Nippon Oil and Fats Co., Ltd.), 50 parts of deionized water and 50 parts of isopropanol, was charged into the reactor in 2 hours, and further a polymerization reaction was effected for 7 hours. The resulting solution was a transparent solution containing 19% of a peroxy bond-containing polymer and having a viscosity of 1.5 poises at 25° C.

(4-2) Production of a graft copolymer:

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In a reactor equipped with a thermometer, a stirrer and a reflux cooler, a mixed solution (VIII) consisting of 100 parts of the isopropanol/water solution containing the peroxy bond-containing polymer and obtained in the above described Step 4-1 and 10 parts of butyl methacrylate was heated at 110° C for 7 hours under pressure while introducing nitrogen gas into the reactor, to effect a graft polymerization reaction. The resulting solution was a white translucent solution containing 26% of a graft copolymer and having a viscosity of 1.3 poises at 25° C.

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Reference example 5

(Production of a hydrophilic and hydrophobic block copolymer)

(5-1) Production of a peroxy bond-containing polymer:

Into a reactor equipped with a thermometer, a stirrer and a reflux cooler was charged 90 parts of N,N-dimethylformamide, and while introducing nitrogen gas into the reactor and heating the reaction system at 70 °C, a mixed solution (IX) consisting of

N,N-dimethylformamide : 30 parts
 styrene : 30 parts
 and

$$\text{—}\overset{\text{O}}{\parallel}\text{C}(\text{CH}_2)_4\overset{\text{O}}{\parallel}\text{CO}(\text{CH}_2)_2\overset{\text{O}}{\parallel}\text{OC}(\text{CH}_2)_4\overset{\text{O}}{\parallel}\text{COO}\text{—}\}_{12}$$
 : 6 parts

was charged into the reactor in 2 hours, and further a polymerization reaction was effected for 3 hours. The resulting solution was a transparent solution containing 23.1% of a peroxy bond-containing polymer and having a viscosity of 2.3 poises at 25 °C.

(5-2) Production of a block copolymer:

In a reactor equipped with a thermometer, a stirrer and a reflux cooler, a mixed solution (X) consisting of 200 parts of the N,N-dimethylformamide solution containing the peroxy bond-containing polymer and obtained in the above described Step 5-1, 100 parts of dimethylformamide and 30 parts of sodium 2-methacrylamide-2-methylpropanesulfonate was heated at 70 °C for 8 hours while introducing nitrogen gas into the reactor, to effect a block polymerization reaction. The resulting solution was a white translucent solution containing 23% of a block copolymer and having a viscosity of 0.3 poise at 25 °C.

Reference example 6

(Production of a hydrophilic and hydrophobic random copolymer)

Into a reactor equipped with a thermometer, a stirrer and a reflux cooler was charged 80 parts of methyl cellosolve, and while introducing nitrogen gas into the reactor and heating the reaction system at 70 °C, a mixed solution consisting of

methyl cellosolve :	20 parts
2-hydroxyethyl methacrylate :	15 parts
methyl methacrylate :	17 parts
N-methylolacrylamide :	3 parts
and	
azoisobutyronitrile :	3 parts

was charged into the reactor in 2 hours, and further a copolymerization reaction was effected for 8 hours. The resulting solution was a transparent solution containing 29.5% of a random copolymer and having a

viscosity of 3.0 poises at 25° C.

Examples 1-7 and Comparative examples 1-3

5 Anti-fogging resin film-forming compositions were produced by the use of the polymers produced in Reference examples 1-6 according to the compounding recipes shown in the following Table 1, and each of the compositions was applied on a matrix under a condition shown in Table 1 such that the composition would be formed into a coating film having a thickness of 5 μ m after dried. The matrix is as follows. The
10 matrix used in Examples 1 and 4 is polymethyl methacrylate, that used in Examples 2, 3 and 7 and Comparative examples 1-3 is polycarbonate and that used in Examples 5 and 6 is polyethylene terephthalate. The matrix used in Examples 1-4 and 7 and Comparative examples 1-3 is a transparent sheet, and that used in Examples 5 and 6 is a transparent film.

The test results of the above obtained coating films are shown in the following Table 2.

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Table 1

	Example							Comparative example		
	1	2	3	4	5	6	7	1	2	3
Block copolymer (1-2)	100					100				
ditto (2-2)		100					100	100		
Graft copolymer (3-2)			100							
ditto (4-2)				100						
Block copolymer (5-2)					100					
Random copolymer (6)									100	100
Nonion S-4 1)	5									
Nonion NS-212 2)		3					3		3	3
Newrex R 3)						5				
Rapisol B-80 4)			6				6			6
Cation AB 5)				5						
Anon BF 6)					7					
p-Toluenesulfonic acid		1	1			1	1	1	1	1
Cymel 325 7)						3				
Silane coupling agent (KBM 403)			5							
Heating condition for film formation	60°C×2hrs	100°C×30min	100°C×30min	60°C×2hrs	150°C×2min	150°C×2min	100°C×30min	100°C×30min	100°C×30min	

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* : The compounding recipe in the table is shown by the weight of solid.

- Note : 1) trademark of polyoxyethylene monostearate sold by Nippon Oil and Fats Co., Ltd.
- 2) trademark of polyoxyethylene nonylphenyl ether sold by Nippon Oil and Fats Co., Ltd.
- 3) trademark of sodium n-dodecylbenzenesulfonate sold by Nippon Oil and Fats Co., Ltd.
- 4) trademark of sodium dioctylsulfosuccinate sold by Nippon Oil and Fats Co., Ltd.
- 5) trademark of octadecyltrimethylammonium chloride sold by Nippon Oil and Fats Co., Ltd.
- 6) trademark of dimethylalkyl(coco)betaine sold by Nippon Oil and Fats Co., Ltd.
- 7) trademark of methoxymethylolmelamine sold by Mitsui Cyanamide Co., Ltd.
- 8) silane coupling agent sold by Shinetsu Chemical Co., Ltd.

Table 2

		Example										Comparative example		
		1	2	3	4	5	6	7	1	2	3			
Anti-fogging property in original state	Expiration test 1)	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙			
	60°C Steam test 2)	>10hrs	>10hrs	>10hrs	>10hrs	>10hrs	>10hrs	>10hrs	5hrs	3hrs	5hrs			
Water-resistance of anti-fogging property 3)	1 hr	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	△	⊙			
	3 hrs	⊙	⊙	⊙	⊙	⊙	⊙	⊙	△	×	△			
	10 hrs	⊙	⊙	⊙	⊙	⊙	⊙	⊙	△	×	×			
Adhesion 4)	Original state	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	△	△			
	After immersed in water	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	×	×			

Note 1) A coating film formed in a constant temperature room kept at 20°C was breathed upon, and the fogged state of the film was observed and judged by the naked eye.

2) A coating film formed in a constant temperature room kept at 20°C was arranged above warm water, kept at 60°C, so as to be exposed to the vapor of the warm water, and the water-resistance of the anti-fogging property of the film was judged by the lapse of time until the film began to be fogged.

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3) A coating film formed in a constant temperature room kept at 20°C was immersed in water kept at 30°C for a predetermined time, and after a lapse of the predetermined time, the coating film was taken out from the water and air-dried. Then, the dried coating film was breathed upon, and the fogged state of the film was observed and judged by the naked eye.

4) A coating film was formed in a constant temperature room kept at 20°C, and with or without an immersion treatment of the coating film, wherein the coating film was immersed in water kept at 30°C for 10 hours and then air-dried, the surface of the coating film was crosscut by means of a cutter knife, a cellophane tape (sold by Nichiban Co., Ltd.) was stuck to the crosscut coating film surface, the crosscut film was peeled off from the matrix in a direction perpendicular to the direction of the adhering interface between the film and the matrix, and the peeled state of the crosscut coating film from the matrix was observed and judged by the naked eye.

The estimation and judging standard in the above tests are as follows:

- ◎ ... excellent (utterly nothing unusual)
- ... good (substantially nothing unusual)
- △ ... fairly good (somewhat poor)
- × ... inferior (utterly poor)

Examples 8-17

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An anti-fogging resin film-forming compositions shown in Table 1 was applied on the surface of a matrix shown in Table 3 such that the composition would be formed into a coating film having a thickness of 5 μm after dried, and was heated and dried under a condition shown in Table 3. The test results of the resulting coating films are shown in Table 3.

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Table 3

	Example									
	8	9	10	11	12	13	14	15	16	17
Anti-fogging composition	Example 1	Example 5	Example 5	Example 5	Example 5	Example 7	Example 7	Example 3	Example 3	Example 3
Material of matrix to be coated i) (transparent or mirror finish)	A	B	C	D	E	F	G	H	I	J
Heating condition for film formation	room temp. x 2 days	80°C x 30 min	80°C x 30 min	60°C x 2 hrs	60°C x 2 hrs	80°C x 30 min	100°C x 30 min	room temp. x 24 hrs	room temp. x 24 hrs	room temp. x 24 hrs
Anti-fogging property in original state	Expiraton test	>10 hrs	>10 hrs	>10 hrs	>10 hrs	>10 hrs	>10 hrs	>10 hrs	>10 hrs	>10 hrs
Water-resistance of anti-fogging property	1 hr	○	○	○	○	○	○	○	○	○
	3 hrs	○	○	○	○	○	○	○	○	○
	10 hrs	○	○	○	○	○	○	○	○	○
Adhesion	Original state	○	○	○	○	○	○	○	○	○
	After immersed in water	○	○	○	○	○	○	○	○	○

Note 1) A : polyvinyl chloride
 B : polystyrene
 C : AS (acrylonitrile-styrene copolymer resin)
 D : ABS resin
 E : SBS (styrene-butadiene copolymer resin)
 F : polyacetate
 G : poly(diethylene glycol-diallyl carbonate)
 H : inorganic glass
 I : aluminum (mirror finish)
 J : stainless steel (mirror finish)

The evaluation method of the performance of coating film and the estimation and judging standard of the performance are the same as those in Table 2.

Reference examples 7-21

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(Production of block copolymers)

10 Into a reactor equipped with a thermometer, a stirrer and a reflux cooler was charged 100 parts of methyl cellosolve, and while introducing nitrogen gas into the reactor and heating the reaction system at 70° C, a mixed solution consisting of

15	methyl cellosolve :	90 parts
	a (meth)acrylamide-type compound :	S parts
	a monomer selected from Group A :	T parts
	a hydrophilic monomer :	U parts
	and	
	$\{ \text{CO}(\text{CH}_2)_4 \text{COO}(\text{C}_2\text{H}_4\text{O})_3 \text{CO}(\text{CH}_2)_4 \text{COO} \}_{10}$:	12 parts

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was charged into the reactor in 2 hours, and further a polymerization reaction was effected for 2 hours. Then, a mixed solution consisting of

25	methyl cellosolve :	60 parts
	a monomer selected from Group A :	V parts
	and	
	a hydrophobic monomer :	W parts

30 was charged into the reactor in 30 minutes, and further a polymerization reaction was effected at 75° C for hours. The numerical values of the above described parts of S-W, and the results of polymerization reactions are shown in Tables 4 and 5.

35 Reference examples 22-24

(Production of random copolymers)

40 Into a reactor equipped with a thermometer, a stirrer and a reflux cooler was charged 150 parts of methyl cellosolve, and while introducing nitrogen gas into the reactor and heating the reaction system at 70° C, a mixed solution consisting of

45	methyl cellosolve :	100 parts
	a (meth)acrylamide-type compound :	S parts
	a monomer selected from Group A :	T parts
	a hydrophilic monomer :	U parts
	a monomer selected from group A :	V parts
50	a hydrophobic monomer :	W parts
	and	
	$\text{CH}_3\text{C}(\text{CH}_3)_2\text{OOCOC}(\text{CH}_3)_3$:	3 parts

55 was charged into the reactor in 2 hours, and further a copolymerization reaction was effected for 5 hours. The numerical values of the above described parts of S-W, and the results of the polymerization reactions are shown in Table 5.

Table 4

	Reference example	7	8	9	10	11	12	13	14	15
5	S	(1)	20	14	5	14	20	-	-	-
		(2)	-	-	-	-	18	12	18	12
		(3)	-	-	-	-	-	-	-	-
10	T	(4)	2	6	8	-	4	6	6	-
		(5)	-	-	-	8	-	-	-	-
	U	(6)	28	50	77	48	12	36	62	34
15		(7)	-	-	-	-	14	-	-	10
	V	(8)	1	3	4	-	2	3	3	-
		(5)	-	-	-	8	-	-	8	-
	W	(9)	49	27	6	22	25	37	17	32
20		(10)	-	-	-	-	23	-	-	2
	Solid content		30	30	30	30	30	30	30	30
25	Viscosity "		4	4	5	4	4	4	5	4

Table 5

	Reference example	16	17	18	19	20	21	22	23	24
30	S	(1)	-	-	6	-	-	14	14	-
		(2)	-	-	-	-	-	-	18	-
35		(3)	28	10	-	3	-	-	-	10
	T	(4)	6	8	4	-	6	-	6	6
		(5)	-	-	-	3	-	-	-	-
40	U	(6)	36	60	20	9	59	56	50	36
		(7)	-	12	-	-	5	-	-	12
	V	(8)	3	4	2	-	3	-	3	3
45		(5)	-	-	-	3	-	-	-	-
	W	(9)	27	6	55	82	27	30	27	37
		(10)	-	-	13	-	-	-	-	-
50	Solid content		30	30	30	30	30	30	28	28
	Viscosity "		4	5	4	3	4	5	4	4

55 The marks used in the above described Tables 4 and 5 have the following meanings.
 (1): N,N-dimethylacrylamide
 (2): N,N-dimethylaminopropylmethacrylamide
 (3): acryloylmorpholine

- (4): glycidyl methacrylate
 (5): N-methylolacrylamide
 (6): 2-hydroxyethyl methacrylate
 (7): mono(2-hydroxyethyl methacrylate)acid phosphate
 (8): acrylic acid
 (9): methyl methacrylate
 (10): isobutyl methacrylate
 * : solid content (% by weight)
 ~ : viscosity (P) at 25 °C

Examples 18-28 and Comparative examples 4-12

Each of all the polymers produced in Reference examples 7-24 was diluted with methyl cellosolve such that the resulting methyl cellosolve solution contained 20% by weight of the solid of the polymer, and then the methyl cellosolve solution was mixed with a surfactant shown in Tables 6 and 7 to produce an anti-fogging coating composition. Then, the composition was applied on a matrix by means of a bar coater such that the composition would be formed into a film having a thickness of 5 μ m after dried, and the coated composition was heated and dried under a condition shown in Tables 6 and 7. Various tests shown in Tables 8-11 of the coated matrix were effected.

Table 6

Example	Polymer (parts)	Surfactant (parts)	Matrix	Curing condition
Example 18	Reference example 7, 100	(a) 2.0	PC	(1)
		(c) 3.0		
Example 19	Reference example 8, 100	(b) 0.5	PC	(1)
		(e) 0.3		
Example 20	Reference example 9, 100	(c) 0.3	PC	(1)
Example 21	Reference example 10, 100	(b) 0.5	AC	(2)
		(d) 0.3		
Example 22	Reference example 11, 100	(c) 4.0	PC	(1)
		(e) 2.0		
Example 23	Reference example 12, 100	(b) 2.0	PC	(1)
		(f) 1.0		
Example 24	Reference example 13, 100	(e) 0.6	PC	(1)
Example 25	Reference example 14, 100	(b) 2.0	AC	(2)
		(c) 2.0		
Example 26	Reference example 15, 100	(a) 0.3	PC	(1)
		(c) 0.3		
Example 27	Reference example 16, 100	(b) 1.5	PC	(1)
		(c) 0.5		
Example 28	Reference example 17, 100	(a) 1.0	PC	(1)
		(d) 0.2		

Table 7

Comparative example	Polymer (parts)	Surfactant (parts)	Matrix	Curing condition
5 4	Reference example 18, 100	(b) 3.0	PC	(1)
		(d) 1.0		
10 5	Reference example 19, 100	(a) 2.0	AC	(2)
		(c) 3.0		
Comparative example 6	Reference example 20, 100	(e) 3.0	PC	(1)
15 7	Reference example 21, 100	(b) 1.0	PC	(1)
		(d) 2.0		
Comparative example 8	Reference example 22, 100	(b) 0.5	PC	(1)
		(c) 3.0		
20 9	Reference example 23, 100	(a) 1.0	PC	(1)
		(c) 1.0		
Comparative example 10	Reference example 24, 100	(a) 0.2	PC	(1)
		(c) 0.2		
25 Comparative example 11	Reference example 8, 100	-	PC	(1)
Comparative example 12	Reference example 13, 100	-	PC	(1)

The marks used in the above Tables 6 and 7 have the following meanings.

Surfactants

- (a) : Nonion NS-212
 (b) : polyoxyethylene octylphenyl ether sold by Nippon Oil and Fats Co., Ltd. under the trademark of Nonion HS-210
 (c) : Newrex R
 (d) : Rapisol B-80
 (e) : Cation AB
 (f) : Anon BF

Matrix

- PC : polycarbonate
 AC : polymethyl methacrylate

Curing condition

- (1) : at 120° C for 30 minutes
 (2) : at 80° C for 60 minutes

The physical properties of the coating films obtained under the above described conditions were evaluated and judged by the following evaluation methods. The obtained results are shown in Tables 8-11.

- (1) Expiration test:

A coating film formed in a constant temperature room kept at 20° C was breathed upon, and the fogged state of the film was judged by the naked eye.

- ⊙ : Film surface is not at all fogged.
 ○ : Water drops spread instantaneously on the film surface.
 Δ : Film surface is somewhat fogged
 x : Film surface is wholly fogged.

5

(2) 40 ° C Steam test:

10 A coating film formed in a constant temperature kept at 20 ° C was exposed to the vapor of warm water kept at 40 ° C, and a lapse of time until the coating film began to be fogged was measured.

(3) 60 ° C Steam test:

15 A coating film formed in a constant temperature room kept at 20 ° C was exposed to the vapor of warm water kept at 60 ° C, and a lapse of time until the coating film began to be fogged was measured.

(4) Water resistance (anti-fogging property):

20

After a coating film was immersed in water kept at 30 ° C for 24 hours, the coating film was air-dried, and then the dried film was subjected to the above described expiration test.

25 (5) Adhesion:

On the surface of a coating film were formed 100 crosscut pieces, which reached the matrix, by means of a cutter knife, and a cellophane adhesive tape (sold by Nichiban Co., Ltd.) was stuck to the crosscut coating film, and then the crosscut coating film was peeled off from the matrix in a direction perpendicular to the direction of the adhering interface between the film and the matrix. The adhesion of the coating film was expressed by the number of crosscut pieces of the coating film remaining on the matrix surface without peeling off therefrom.

35 (6) Heat resistance:

After a coating film was left to stand for 1,000 hours in an incubator kept at 80 ° C, the above described adhesion test was effected.

40

(7) Water resistance (adhesion):

After a coating film was immersed in warm water kept at 70 ° c for 200 hours, the coating film was air-dried, and then the dried film was subjected to the above described adhesion test.

45

(8) Hardness:

A pencil scratch test was effected according to JIS K 5400.

- 50 ○ : equal to or harder than the hardness 2H of lead pencil
 x : softer than the hardness 2H of lead pencil

(9) Water resistance (strength of coating film):

55

After a coating film was immersed in water kept at 30 ° C for 24 hours, the appearance of the film was observed and judged by the naked eye.

- : no change in the appearance

x : The appearance was somewhat charged.

Table 8

Example	Anti-fogging property			
	Expiration test	40° C Steam test	60° C Steam test	Water resistance
Example 18	⊙	at least 5 hours	at least 5 hours	Δ
Example 19	○	at least 5 hours	at least 5 hours	Δ
Example 20	○	at least 5 hours	at least 5 hours	○
Example 21	⊙	at least 5 hours	at least 5 hours	Δ
Example 22	⊙	at least 5 hours	at least 5 hours	Δ
Example 23	⊙	at least 5 hours	at least 5 hours	Δ
Example 24	○	at least 5 hours	at least 5 hours	○
Example 25	⊙	at least 5 hours	at least 5 hours	Δ
Example 26	⊙	at least 5 hours	at least 5 hours	○
Example 27	⊙	at least 5 hours	at least 5 hours	Δ
Example 28	⊙	at least 5 hours	at least 5 hours	○

Table 9

Example	Adhesion			Strength of coating film	
	Original state	Heat resistance	Water resistance	Hardness	Water resistance
Example 18	(a)	(a)	(a)	○	○
Example 19	(a)	(a)	(a)	○	○
Example 20	(a)	(a)	(a)	○	○
Example 21	(a)	(a)	(a)	○	○
Example 22	(a)	(a)	(a)	○	○
Example 23	(a)	(a)	(a)	○	○
Example 24	(a)	(a)	(a)	○	○
Example 25	(a)	(a)	(a)	○	○
Example 26	(a)	(a)	(a)	○	○
Example 27	(a)	(a)	(a)	○	○
Example 28	(a)	(a)	(a)	○	○

Table 10

Comparative example	Anti-fogging property			
	Expiration test	40 ° C Steam test	60 ° C Steam test	Water resistance
Comparative example 4	Δ	3 hours	2 hours	×
Comparative example 5	Δ	2 hours	1 hour	×
Comparative example 6	⊙	at least 5 hours	4 hours	Δ
Comparative example 7	⊙	at least 5 hours	4 hours	×
Comparative example 8	⊙	at least 5 hours	4 hours	Δ
Comparative example 9	○	at least 5 hours	at least 5 hours	Δ
Comparative example 10	○	4 hours	3 hours	Δ
Comparative example 11	×	just after	just after	×
Comparative example 12	×	just after	just after	×

Table 11

Comparative example	Adhesion			Strength of coating film	
	Original state	Heat resistance	Water resistance	Hardness	Water resistance
Comparative example 4	(a)	(a)	(a)	○	○
Comparative example 5	(a)	(a)	(a)	○	○
Comparative example 6	(a)	(d)	(d)	○	○
Comparative example 7	(a)	(a)	(a)	×	×
Comparative example 8	(b)	(d)	(d)	○	○
Comparative example 9	(c)	(d)	(d)	○	○
Comparative example 10	(b)	(d)	(d)	○	○
Comparative example 11	(a)	(a)	(a)	○	○
Comparative example 12	(a)	(a)	(a)	○	○

The marks used in the above described Tables 8-11 have the following meanings.

Adhesion test:

(a) : 100/100

(b) : 30/100

(c) : 15/100

(d) : 0/100

Reference examples 25-34

(Production of block copolymers)

Into a reactor equipped with a thermometer, a stirrer and a reflux cooler was charged 230 parts of methyl cellosolve, and while introducing nitrogen gas into the reactor and heating the reaction system at 72° c, a mixed solution consisting of

5	methyl cellosolve :	100 parts
	glycidyl methacrylate or N-methylolacrylamide :	A parts
	hydroxyalkyl (meth)acrylate :	B parts
10	a monomer selected from acrylamide, N-monomethylacrylamide, N,N-dimethylacrylamide, acryloylmorpholine and N-vinylpyrrolidone :	C parts
15	and $\{ \text{CO}(\text{CH}_2)_4 \text{COO}(\text{C}_2\text{H}_4\text{O})_3 (\text{CO}(\text{CH}_2)_4 \text{COO})_{10} \}$:	20 parts

was charged into the reactor in 2 hours, and further a polymerization reaction was effected for 2 hours.
20 Then, a mixed solution consisting of

25	methyl cellosolve :	285 parts
	lower alkyl (meth)acrylate :	D parts
	and (meth)acrylic acid :	E parts

was charged into the reactor in 30 minutes, and further a polymerization reaction was effected at 75° C for hours. The numerical values of the above described parts of A E are shown in Tables 12 and 13 together
30 with the results of the polymerization reactions.

Reference examples 35-40

35

(Production of graft copolymers)

Into a reactor equipped with a thermometer, a stirrer and a reflux cooler was charged 230 parts of methyl cellosolve, and while introducing nitrogen gas into the reactor and heating the reaction system at
40 85° C, a mixed solution consisting of

45	Perbutyl O :	2.3 parts
	t-butylperoxy methacryloyloxyethyl carbonate used as a radically copolymerizable organic peroxide :	6.0 parts
	methyl cellosolve :	100 parts
50	glycidyl (meth)acrylate or N-methylolacrylamide :	A parts
	hydroxyalkyl (meth)acrylate :	B parts
55	and a monomer selected from acrylamide, N-monomethylacrylamide, N,N-dimethylacrylamide, acryloylmorpholine and N-vinylpyrrolidone :	C parts

was charged into the reactor in 2 hours, and further a polymerization reaction was effected for 7 hours.

Then, the reaction solution was heated up to 110° C, and a mixed solution consisting of

methyl cellosolve :	285 parts
lower alkyl (meth)acrylate :	D parts
and	
(meth)acrylic acid :	E parts

5

was charged into the reactor in 30 minutes, and further a polymerization reaction was effected at 110° C for 7 hours to produce a graft copolymer. The numerical values of the above described parts of A-E and the results of the polymerization reactions are shown in Table 13.

10

Reference examples 41-44

15

(Production of random copolymers)

Into a reactor equipped with a thermometer, a stirrer and a reflux cooler was charged 230 parts of methyl cellosolve, and while introducing nitrogen gas into the reactor and heating the reaction system at 85° C, a mixed solution consisting of

20

Perbutyl O :	2.3 parts
methyl cellosolve :	370 parts
glycidyl (meth)acrylate or N-methylolacrylamide :	A parts
hydroxyalkyl (meth)acrylate :	B parts
a monomer selected from acrylamide, N-monomethylacrylamide, N,N-dimethylacrylamide, acryloylmorpholine and N-vinylpyrrolidone :	C parts
lower alkyl (meth)acrylate :	D parts
and	
(meth)acrylic acid :	E parts

25

30

35

40

was charged into the reactor in 3 hours, and further a polymerization reaction was effected for 7 hours. The numerical values of the above described parts of A-E and the results of the polymerization reactions are shown in Table 13.

45

50

55

Table 12

Reference example		25	26	27	28	29	30	31	32	33	34
A	(1)	6	-	-	9	18	-	12	-	9	30
	(2)	-	12	25	-	-	6	-	25	-	-
B	(3)	90	-	-	78	-	-	66	-	-	60
	(4)	-	66	-	-	55	-	-	43	-	-
	(5)	-	-	43	-	-	90	-	-	78	-
C	(6)	4	-	-	-	-	4	-	-	-	-
	(7)	-	22	-	-	-	-	22	-	-	-
	(8)	-	-	32	-	-	-	-	32	-	-
	(9)	-	-	-	13	-	-	-	-	13	-
	(10)	-	-	-	-	27	-	-	-	-	10
D	(11)	85	-	-	76	-	-	67	-	-	40
	(12)	-	67	-	-	60	-	-	50	-	-
	(13)	-	-	50	-	-	85	-	-	76	-
E	(14)	15	-	50	-	40	-	33	-	24	-
	(15)	-	33	-	24	-	15	-	50	-	60
Solid content *		26	26	26	26	26	26	26	26	26	26
Viscosity **		6	6	7	7	5	5	4.5	9	3.5	7

Table 13

Reference example		35	36	37	38	39	40	41	42	43	44
A	(1)	18	-	12	-	9	-	6	-	12	-
	(2)	-	6	-	25	-	6	-	12	-	25
B	(3)	-	-	66	-	-	14	90	-	66	-
	(4)	55	-	-	43	-	-	-	66	-	43
	(5)	-	90	-	-	78	-	-	-	-	-
C	(6)	27	-	-	-	-	80	4	-	-	-
	(7)	-	4	-	-	-	-	-	22	-	-
	(8)	-	-	22	-	-	-	-	-	22	-
	(9)	-	-	-	32	-	-	-	-	-	32
	(10)	-	-	-	-	13	-	-	-	-	-
D	(11)	-	-	67	-	-	85	85	-	67	-
	(12)	60	-	-	50	-	-	-	67	-	50
	(13)	-	85	-	-	76	-	-	-	-	-
E	(14)	40	-	33	-	24	-	15	-	33	-
	(15)	-	15	-	50	-	15	-	33	-	50
Solid content		25	25	25	25	25	25	25	25	25	25
Viscosity		5	4.5	4	3	6	6	4	4	3.5	3

The marks used in the above described Tables 12 and 13 have the following meanings.

- (1): glycidyl (meth)acrylate
- (2): N-methylolacrylamide
- (3): 2-hydroxyethyl methacrylate
- (4): 2-hydroxyethyl acrylate
- (5): 2-hydroxypropyl methacrylate
- (6): acrylamide
- (7): N-monomethylacrylamide
- (8): N,N-dimethylacrylamide
- (9): N-acryloylmorpholine
- (10): N-vinylpyrrolidone
- (11): methyl methacrylate
- (12): ethyl acrylate
- (13): ethyl methacrylate
- (14): methacrylic acid
- (15): acrylic acid
- [°]: solid content (% by weight)
- [°]: viscosity (P) at 25° C

Examples 29-47 and Comparative examples 13-22

A polymer produced in Reference examples 25-44 was compounded with a surfactant shown in Tables 14-16, and the resulting coating composition was applied on a polyester film (trademark: Polyethylene Terephthalate Film E-5101, sold by Tōyō Bōsei Co., Ltd.), and the applied composition was heated and cured under a condition shown in Tables 14-16. The resulting coating film formed on the polyester film was

subjected to various tests shown in Tables 17-19.

Table 14

Example	Polymer (parts)	Surfactant (parts)	Heating condition for film formation
Example 29	Reference example 25, 100	(a) 7.0	150 ° C, 2 min.
Example 30	Reference example 26, 100	(b) 10.0	130 ° C, 2 min.
		(g) 1.0	
Example 31	Reference example 27, 100	(c) 6.0	130 ° C, 2 min.
		(g) 1.0	
Example 32	Reference example 28, 100	(d) 8.0	150 ° C, 2 min.
Example 33	Reference example 29, 100	(e) 4.0	150 ° C, 2 min.
Example 34	Reference example 30, 100	(f) 7.0	120 ° C, 3 min.
		(g) 1.0	
Example 35	Reference example 31, 100	(a) 10.0	170 ° C, 1 min.
Example 36	Reference example 32, 100	(b) 10.0	150 ° C, 1 min.
		(g) 1.0	
Example 37	Reference example 33, 100	(c) 5.0	190 ° C, 30 sec.
Example 38	Reference example 35, 100	(d) 5.0	160 ° C, 1 min.

Table 15

Example	Polymer (parts)	Surfactant (parts)	Heating condition for film formation
Example 39	Reference example 36, 100	(e) 5.0	140 ° C, 1 min.
		(g) 1.0	
Example 40	Reference example 37, 100	(f) 5.0	150 ° C, 2 min.
Example 41	Reference example 25, 100	(e) 3.0	170 ° C, 1 min.
Example 42	Reference example 26, 100	(d) 3.0	140 ° C, 1 min.
		(g) 1.0	
Example 43	Reference example 27, 100	(c) 15.0	150 ° C, 1 min.
		(g) 1.0	
Example 44	Reference example 38, 100	(h) 12.0	120 ° C, 3 min.
		(g) 1.0	
Example 45	Reference example 39, 100	(k) 8.0	170 ° C, 1 min.
Example 46	Reference example 38, 100	(b) 2.0	130 ° C, 2 min.
		(j) 9.0	
Example 47	Reference example 39, 100	(d) 1.0	150 ° C, 2 min.
		(i) 10.0	

Table 16

Comparative example	Polymer (parts)	Surfactant (parts)	Heating condition for film formation
Comparative example 13	Reference example 34, 100	(d) 7.0	150 °C, 2 min.
Comparative example 14	Reference example 40, 100	(b) 3.0 (g) 1.0	130 °C, 2 min.
Comparative example 15	Reference example 41, 100	(a) 7.0	150 °C, 2 min.
Comparative example 16	Reference example 42, 100	(b) 10.0 (g) 1.0	130 °C, 2 min.
Comparative example 17	Reference example 43, 100	(e) 3.0	170 °C, 1 min.
Comparative example 18	Reference example 44, 100	(h) 12.0 (g) 1.0	120 °C, 3 min.
Comparative example 19	Reference example 34, 100	(f) 7.0	170 °C, 1 min.
Comparative example 20	Reference example 40, 100	(c) 6.0 (g) 1.0	120 °C, 3 min.
Comparative example 21	Reference example 39, 100	-	170 °C, 1 min.
Comparative example 22	Reference example 41, 100	-	150 °C, 2 min.

The marks of the surfactants used in the above described Tables 14-16 have the following meanings.

- (a) : Nonion S-4
- (b) : Nonion NS-212
- (c) : Newrex R
- (d) : Rapisol B-80
- (de) : Cation AB
- (f) : Anon BF
- (g) : p-toluenesulfonic acid
- (h) : polyoxyethylene-polyoxypropylene condensate (trademark: Pluronic F-68, sold by Asahi Denka Kōgyō Co., Ltd.)
- (i) : polyoxyethylene nonylphenyl ether (trademark: Noigen EA-120, sold by Dai-ichi Kōgyō Seiyaku Co., Ltd.)
- (j) : dialkyl sulfosuccinate (trademark: Neocol SW, sold by Dai-ichi Kōgyō Seiyaku Co., Ltd.,
- (k) : stearyl betaine (trademark: Bistar MS, sold by Matsumoto Yushi Co., Ltd.)

Table 17

Example	Anti-fogging property in original state		Durability of anti-fogging property (3)	Water-resistance of anti-fogging property (4)			Adhesion of coating film (8)	Strength of coating film (9)
	(1)	(2)		(5)	(6)	(7)		
Example 29	◎	◎	>5	◎	◎	○	◎	◎
Example 30	◎	◎	>5	◎	◎	◎	◎	◎
Example 31	◎	◎	>5	◎	◎	○	◎	◎
Example 32	◎	◎	>5	◎	◎	◎	◎	◎
Example 33	◎	◎	4	◎	◎	○	◎	◎
Example 34	◎	◎	4	◎	◎	○	◎	◎
Example 35	◎	◎	4	◎	○	○	◎	◎
Example 36	◎	◎	>5	◎	◎	◎	◎	○
Example 37	◎	◎	3	◎	○	○	◎	◎
Example 38	◎	◎	>5	◎	◎	◎	◎	◎

Table 18

Example	Anti-fogging property in original state		Durability of anti-fogging property (3)	Water-resistance of anti-fogging property (4)			Adhesion of coating film (8)	Strength of coating film (9)
	(1)	(2)		(5)	(6)	(7)		
Example 39	◎	◎	>5	◎	◎	○	◎	◎
Example 40	◎	◎	4	◎	◎	○	◎	◎
Example 41	◎	◎	5	◎	◎	○	◎	◎
Example 42	◎	◎	5	◎	◎	○	◎	◎
Example 43	◎	◎	5	◎	◎	○	◎	◎
Example 44	◎	◎	3	◎	○	○	◎	◎
Example 45	◎	◎	>5	◎	◎	○	◎	◎
Example 46	◎	◎	5	◎	○	○	◎	◎
Example 47	◎	◎	>5	◎	◎	◎	◎	◎

Table 19

Comparative example	Anti-fogging property in original state		Durability of anti-fogging property (3)	Water-resistance of anti-fogging property (4)			Adhesion of coating film (8)	Strength of coating film (9)
	(1)	(2)		(5)	(6)	(7)		
Comparative example 13	◎	◎	<1	○	x	x	◎	◎
Comparative example 14	◎	◎	>5	◎	◎	◎	△	x
Comparative example 15	○	○	<1	○	△	x	x	x
Comparative example 16	○	○	<1	○	△	x	x	x
Comparative example 17	○	△	instantaneous	x	x	x	◎	x
Comparative example 18	△	x	instantaneous	x	x	x	◎	△
Comparative example 19	◎	◎	<1	○	x	x	◎	◎
Comparative example 20	◎	◎	>5	◎	◎	◎	x	x
Comparative example 21	◎	◎	3	○	△	x	◎	◎
Comparative example 22	x	x	instantaneous	x	x	x	x	x

The marks used in the above described Tables 17-19 have the following meanings.

- (1) : A coating film formed in a constant temperature room kept at 20 °C was breathed upon, and the wetted state of the coating film was observed and judged by the naked eye.
- (2) : A coating film formed in a constant temperature room kept at 20 °C was horizontally arranged above warm water, kept at 60 °C, so as to be exposed to the vapor of the warm water, and after the coating film was left to stand for 1 minute, the wetted state of the film was observed and judged by the naked eye.
- (3) : A coating film formed in a constant temperature room kept at 20 °C was perpendicularly arranged under a tightly closed state on warm water, kept at 60 °C, so as to be exposed to the vapor of the warm water, and the durability of the anti-fogging property of the coating film was judged by a lapse of time until the film began to be fogged.
- (4) : A coating film formed in a constant temperature room kept at 20 °C was immersed in water kept at 30 °C for predetermined times, taken out from the water every predetermined times, and air-dried, and then after the coating film was breathed upon, the fogged state of the film was observed and judged by the naked eye.
- (5) : after 1 hour
- (6) : after 3 hours
- (7) : after 10 hours
- (8) : The surface of a coating film formed in a constant temperature room kept at 20 °C was crosscut by means of a cutter knife, a cellophane tape (sold by Nichiban Co., Ltd.) was stuck to the crosscut coating film, the crosscut film was peeled off from the matrix in a direction perpendicular to that of the adhering interface between the crosscut film and the matrix, and the peeled state of the crosscut film from the matrix was observed and judged by the naked eye.
- (9) : After coating film formed in a constant temperature room kept at 20 °C was immersed in water kept at 30 °C for 10 hours, the coating film was taken out from the water and rubbed with a finger, and the cracked state and the peeled state of the film from the substrate were observed and judged by the naked eye.

The estimation and judging standard of the performance of the coating film is as follows.

- ⊙ : utterly nothing unusual
- : substantially nothing unusual
- △ : somewhat poor
- × : utterly poor

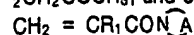
Instantaneous : A coating film begins to be fogged simultaneously with the starting of the judging operation.

- As described above, it has been proved that the anti-fogging resin film-forming composition of the present invention can form a coating film having high durability of anti-fogging property, high strength and high adhesion in well-balanced state. On the contrary, a coating composition using a block or graft copolymer having a composition outside the range specifically limited in the present invention or using a random copolymer is poor in any one of the above described 3 properties, and is unsatisfactory in the performance as an anti-fogging resin film-forming composition.

40 Claims

1. An anti-fogging resin film-forming composition, comprising at least one copolymer selected from block copolymers and graft copolymers, and a surfactant, each of said block copolymer and said graft copolymer consisting of a hydrophilic polymer segment and a hydrophobic polymer segment.
 2. An anti-fogging resin film-forming composition according to claim 1, wherein said block copolymer consists of a hydrophilic polymer segment and a hydrophobic polymer segment, said hydrophilic polymer segment being formed of 1-40% by weight of at least one of N-substituted or non-substituted (meth)acrylamide-type compounds represented by the following general formula (I) or (II), 1-20% by weight of at least one monomer selected from the group (referred to as Group A) consisting of monomers having a crosslinkable functional group of any one of glycidyl group, N-methylol group, N-methylether group, carboxyl group and acid anhydride, and 40-98% by weight of at least one of hydrophilic monomers copolymerizable with the above described (meth)acrylamide-type compound and the monomer of the above described Group A, said hydrophobic polymer segment being formed of 1-40% by weight of at least one monomer selected from the monomers of Group A, and 60-99% by weight of at least one hydrophobic monomer copolymerizable with the monomer of Group A, the weight ratio of the hydrophilic polymer segment to the hydrophobic polymer segment being within the range of 50/50-95/5, said general formula (I) being
- $$\text{CH}_2 = \text{CR}_1\text{CONR}_2\text{R}_3$$

wherein R_1 and R_2 represent hydrogen atoms or methyl groups; and R_3 represents hydrogen atom, methyl group, ethyl group, n-propyl group, isopropyl group, N,N-dimethylaminopropyl group or $-C(CH_3)_2CH_2COCH_3$, and said general formula (II) being



- 5 wherein R_1 represents hydrogen atom or methyl group; and A represents $-(CH_2)_n-$ (wherein n is a positive integer of 4 or 5) or $-(CH_2)_2-O-(CH_2)_2-$.

3. An anti-fogging resin-forming composition according to claim 1, wherein said block or graft copolymer consists of a hydrophilic polymer segment formed of 6-25% by weight of a monomer of glycidyl (meth)acrylate or N-methylolacrylamide, 43-90% by weight of hydroxyalkyl (meth)acrylate, and 4-32% by
10 weight of a monomer selected from the group consisting of acrylamide, N-monomethylacrylamide, N,N-dimethylacrylamide, N-acryloylmorpholine and N-vinylpyrrolidone, and a hydrophobic polymer segment formed of 50-85% by weight of lower alkyl (meth)acrylate and 15-50% by weight of (meth)acrylic acid.

4. An anti-fogging resin film-forming composition according to claim 1, wherein said surfactant is nonionic surfactant or anionic surfactant.

15 5. An anti-fogging resin film-forming composition according to claim 1, wherein said surfactant is a combination of nonionic surfactant and anionic surfactant.

6. An anti-fogging resin film-forming composition according to claim 1, which contains 0.1-10 parts by weight of the surfactant based on 100 parts by weight of the copolymer.

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